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Reconciling Urban VOC/NOx (Volatile Organic Compounds/NOx) Emission Inventories with Ambient Concentration Data

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RECONCILING URBAN VOC/NOX EMISSION INVENTORIES WITH AMBIENT CONCENTRATION DATA

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16. ABSTRACT

A review of the current state of emission inventories of VOC and No_x data compiled for urban areas in the U.S. is presented. The study reveal great differences in the gross emission magnitudes when compared with corresponding ambient air concentration data. The VOC emissions data are in general, shown to be underestimated by factors exceeding 3 or more for most cities. Also, large differences are apparent when different methods of preparation are applied to develop the emissions inventory. At this time there is no acceptable method to check the accuracy of the overall emission output from these major area sources. The mass balance approach to determining the urban area source strength is in principle, able to provide an absolute measure of such emissions rate. The method is reviewed, and an approach to conducting a feasibility study is discussed. The aggregated emission from urban areas is determined from measurements of excess crosswind and vertically integrated pollutant concentration over background in the urban plume just downwind of the emissions area. Adjustments for pollutant transformation and deposition losses upwind of the sampling plane, if determined from model calculations, will introduce a certain amount of model noise. Therefore, the only limits to the accuracy of the derived emission will be the sum of observational and modeling uncertainties.

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INTRODUCTION

The problems of acidic deposition and photochemical smog, among others, originate with the emission of the precursor species SO_2, NO_x, and a myriad of volatile organic compounds (VOC). These precursors are chemically transformed in the atmosphere to acidic products (e.g., sulfuric acid, nitric acid, organic acids), visibility reducing aerosols (e.g., sulfates), and to such noxious and harmful products as O_3 and PAN (an organic nitrate). Precursor photochemistry provides the important coupling between the phenomena of acidic deposition and photochemical smog, and is a principal source of non-linearity in the source-receptor relationships pertaining to these two phenomena.

Regulations to mitigate these regional pollution problems are developed after analysis of control strategies and atmospheric modeling to estimate the impacts of the controls. Atmospheric models used in this analysis are regional models which simulate atmospheric dispersion, transformation, and deposition processes. EPA is currently sponsoring two major efforts aimed at development and evaluation of two independent and sophisticated Eulerian models: the Regional Acid Deposition Model (RADM) and the Regional Oxidant Model (ROM). The validity and utility of these models will be determined critically, in part, by the reliability of their input emissions data. An accurate representation of the magnitude and temporal and spatial distribution of the SO_2, NO_x, and VOC emitted into the atmosphere is of central importance to reliable assessment and control of the problems of acidic deposition and local as well as regional oxidant burdening of the atmosphere. Thus, accurate emissions data is crucial to the selection of control strategies and regulations which will effectively mitigate pollution problems.

The National Acid Precipitation Assessment Program's (NAPAP) Task Group on Emissions and Controls has the responsibility for development of anthropogenic precursor emission inventories in support of these and other related research and assessment activities. Traditionally, these anthropogenic inventoring has been developed from the U.S. EPA's National Emissions Data Survey. The accuracy of this database and emissions inventories developed from it is a topic of much debate. Emissions are typically estimated by multiplying an activity or fuel consumption level by an average emission factor. The completeness of this database as well as different assumptions or methodologies for calculating emissions can have a significant impact on the resulting emission estimates.

Because inventories are developed from emissions estimates rather than measurements, there can be no conclusive check on how well the estimated emissions represent actual emissions. There is, however, suggestive evidence based on ambient measurements of nitrogen oxides (NO_x) and nonmethane organic compounds (NMOC) in urban areas that existing VOC emission inventories may be considerably underestimated. This evidence is strengthened by the limitations of the National Emissions Data Survey. Currently, states are not required to report emissions from point sources that emit less than 100 tons per year. In instances were significant quantity of emission may be emitted from smaller sources and when surrogate emission indicators are difficult to quantify, the likelihood of underestimation is high. The ambient measurements which suggest

the likelihood of problems with the emission inventories are themselves point measurements and hence not the best surrogates for urban emissions. Thus an independent means for determining actual emissions is needed to better assess the accuracy of emission inventories.

As a candidate, the mass balance approach in principle, has the potential to provide a meaningful and reliable measure of the actual emissions of any precursor species from an urban area over any given period of time. To date, utilization and studies to demonstrate feasibility of this approach towards determination of emissions rate has not been extensive, however the purpose of this paper is to 1) present emissions and ambient measurement data which support the need for an independent measure of emissions and 2) to discuss pertinent properties and requirements of the mass balance approach as an independent means of determining aggregated source strengths of NO_x and VOC for an urban area. Part of this overview will explore observational requirements for reliable estimates of emissions fluxes with temporal, spatial, and species resolutions consistent with regional modeling emissions requirements. In a companion paper[1], Gillani et al., 1987, describes the mass balance method in greater detail and also discusses the existing data bases from which the mass balance approach will be tested.

EMISSIONS

Recognizing the importance of providing some estimate of the uncertainty associated with emission estimate the Man-Made Sources Task Group of the Interagency Task Force on Acid Precipitation sponsored a workshop on "Accuracy in National Scale Air Pollutant Emissions Data Bases"[2] in January 1984 which addressed many of the difficulties surrounding the question of accuracy in emission estimates. The Workshop viewed accuracy of emissions as a measure of how close the emissions estimate is to the actual emissions value However, since actual emissions are not well known, the task of determining accuracy of the emissions inventory becomes one of estimating the uncertainty surrounding inventory emission estimates. This, in turn, involves quantitative measures of 1) the certainty that the actual emissions value lies between some defined limits, 2) the internal consistency of the emissions estimates, and 3) the bias in emission estimates. An assessment of the internal consistency of the emission estimates through statistical methods and the use of expert teams is discussed in Benkovitz, 1985[3]. That report presents preliminary uncertainty estimates for one component or category of factors that must be evaluated to determine inventory uncertainty for the NAPAP 1980 base year inventory. These preliminary results indicate that area source emission factors and speciation factors for VOC are the components with highest uncertainty, in the range of 100%. Even with improvements in precision of these components the major problem still remaining is to determine how close the emissions estimates are to actual emissions. This is the absolute measure of accuracy of emissions inventories.

The basic information for estimating annual emissions are taken from EPA's National Emissions Data System (NEDS). Primarily the data consist of statistically averaged emission factors and fuel consumption estimates which are used to calculate annual emissions of the five criteria pollutants (TSP, SO_x, NO_x, VOC and CO). Point source emission estimates are based on individual sources or processes whereas area source emissions are based on county level

fuel consumption or activity estimates. Such statistically averaged parameters may not adequately represent the full population of sources. Such inaccuracies in the basic data probably constitute an important source of error in the emission inventories even though the precision of these estimates have been significantly improved in consecutive NAPAP updates. Further uncertainties of the NAPAP inventories used in regional scale models result from the application of spatial, temporal, and species allocation algorithms to annual county and point emissions. For example, countywide area source emissions are allocated to a subcounty grid scale (1/4° longitude by 1/6° latitude); annual emissions estimates are allocated to seasonal, daily and hourly resolution; and total VOC emissions are broken into about a dozen VOC classes specifically corresponding to model chemistry mechanism requirements. Also, several known VOC source categories which were not included in the 1980 emissions are now scheduled for inclusion in the NAPAP 1985 inventory. These include: publically owned treatment works (POTW's), hazardous waste treatment, storage and disposal facilities (TSDF's), fugitive emissions from synthetic organic chemical manufacturing and petroleum refinery operations, bulk terminal and bulk plants, pharmaceutical and synthetic fiber manufacturing, etc. The combined uncertainty from all of these factors is probably quite large, but not quantifiable.

A review of emission inventory development efforts during the past few years provides a startling awareness of the impact of emission inventory updates on the gridded emission estimates used in Eulerian regional scale model development and evaluation activities. To date these emission inventory efforts have primarily focused on providing a 1980 base year inventory. Table I summarizes some of the methodology updates over a four year period. This summary and related emission comparisons shown in Figures 1 thru 4 provide some indication of the impact of methodology changes on successive estimates of the 1980 base year emissions.

The Northeast Corridor Regional Modeling Project (NECRMP) was one of the earliest attempts to provide detailed ozone precursor (VOC, NO_x) emissions required by regional models using nonlinear chemistry mechanisms. Figures 1 and 2 compare 200 grid cells with highest emissions (point and area sources combined) of NO_x and VOC respectively in the Northeastern U.S. The regression lines in both bases show that the NAPAP 4.2 inventory updates have effectively reduced the estimated source strengths of grids that were strongest in the NECRMP data set and raised the estimated strengths of weaker grids. These differences may be attributed to spatial shifts due to use of different census data for spatial allocation or to emission factor differences introduced by the AP-42 emission factor supplement updates. For the most part, the NAPAP values are within a factor of 3 of the corresponding NECRMP estimates. The uncertainties are largest, however, in the NO_x data where discrepancies as large as a factor of 100 occur. Figure 3 compares two successive versions of the NAPAP NO inventory. The bulk of the data shows high correlation; no bias appears, but the magnitude of the outliers raises concern about the accuracy of current emission methodologies. Since motor vehicles typically contribute 50% of the NO_x emissions the update from Mobile 2 emission factors to Mobile 3 emission factors might possibly explain the observed differences. Finally Figure 4 compares the NAPAP 4.2 and 5.3 grid emissions of sulfur dioxide (SO_2). SO_2 emissions are thought to be most accurately estimated because

TABLE I Proposed uncertainties for the NAPAP 1980 base year inventory
from: Benkovitz (1985)

Parameter	Uncertainty Range (%)			
	SO_x	NO_x	VOC	Across all Pollutants
Fuel S content				10
Point source emission factors				
Method 1 (stack tests)	25	25	25	
2 (material balance)	10	25	50	
3 (AP-42 emission factors)				
confidence rating A	10	10	10	
B	25	25	25	
C	50	50	50	
D	75	75	75	
E	100	100	100	
5 (state emission factor)	25	50	50	
4,6,7,0 and blank	100	100	100	
Point source production throughput	15	15	15	
Control equipment efficiency	25	25	25	
Area source emission factors				
Mobile sources	*	50	100	
"Other" sources	25	25	100	
Area Source activity level				
Mobile				25
Other				25
Point source temporal apportionment				
Seasonal profiles	10	10	10	
Daily profiles	25	25	25	
Hourly profiles	50	50	75	
Area sources temporal apportionment				
Seasonal profiles	10	10	10	
Daily profiles	25	25	25	
Hourly profiles	50	50	75	
Area sources spatial apportionment factors	25	25	25	
Chemical speciation factors				
NO/NO_2				25
VOC				100

*Apply same criteria as for point source emission factors.

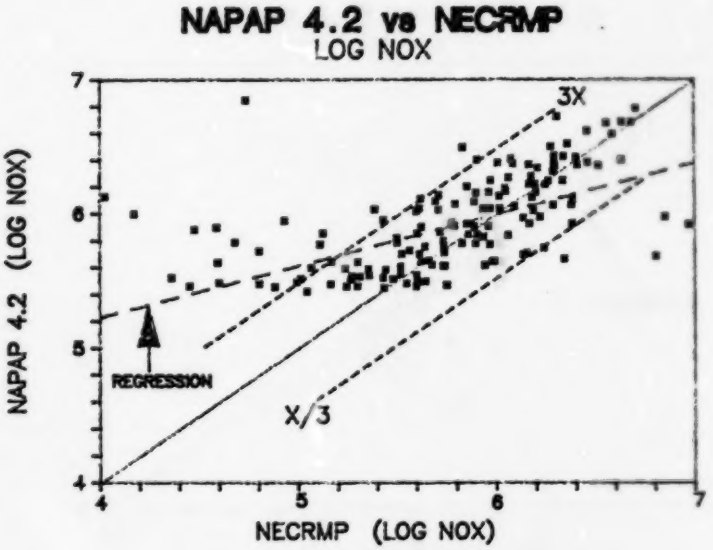

Figure 1. Comparison of NAPAP 4.2 and NECRMP gridded NOX emissions for the 200 strongest source cells in the Northeastern U. S. ROM domain.

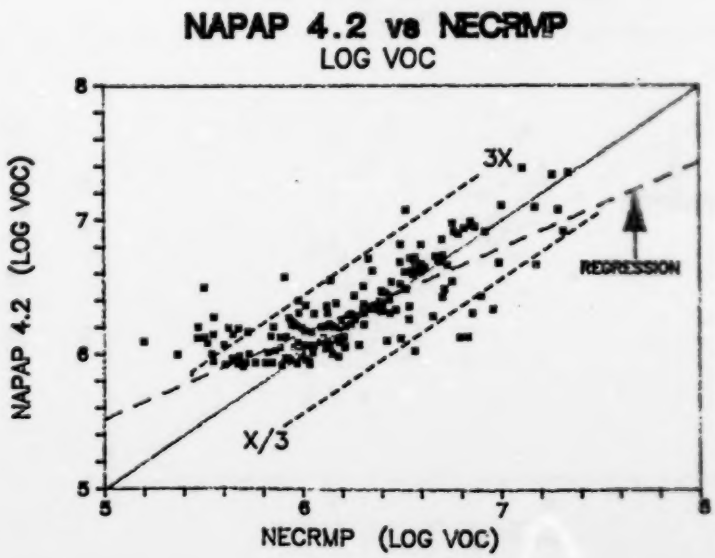

Figure 2. Comparison of NAPAP 4.2 and NECRMP gridded VOC emissions for the 200 strongest source cells in the Northeastern U. S. ROM domain.

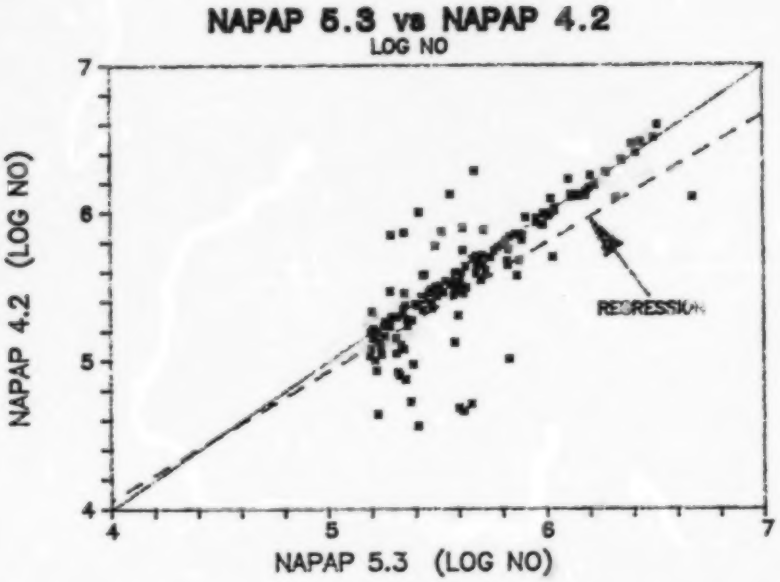

Figure 3. Comparison of NAPAP 5.3 and NAPAP 4.2 gridded NO emissions for the 200 strongest source cells in the Northeastern U.S. ROM domain.

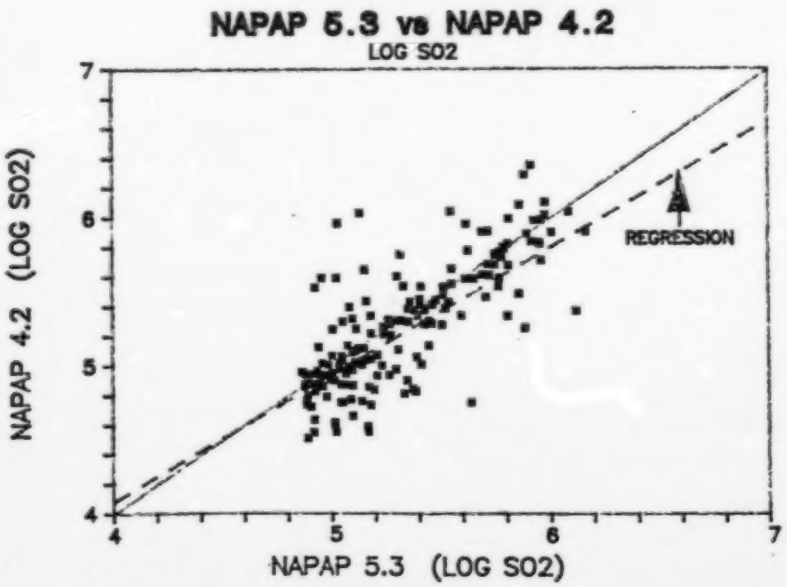

Figure 4. Comparison of NAPAP 5.3 and NAPAP 4.2 gridded SO2 emissions for the 200 strongest source cells in the Northeastern U.S. ROM domain.

the bulk of emissions are generated by utilities and industrial combustion sources whose emissions factors have been more accurately determined. As illustrated, however, even gridded SO_2 emissions exhibit significant differences in the latest NAPAP update. The Eulerian models primarily use emissions in gridded form. While the bias is small, the "noise" level between successive estimates of gridded 1980 base year emissions is a factor of 10. This brings into question the significance of the model calculations themselves because the response of O_3 concentrations to changes in VOC and NO_x emissions is a function of the base emission levels. Therefore, if the estimated base emissions are in error, the simulated response of O_3 concentrations to emissions controls could also be in error.

AMBIENT MEASUREMENTS

There is suggestive evidence based on ambient measurements in urban areas that current emissions inventories, especially of VOC, may be significantly underestimated by as much as a factor of 5 for some urban areas. For example, in a study in Atlanta in July 1981[4] the mean value of the NMOC/NO_x ratio based on ambient measurements in the city was 8.6 compared to the value of 1.5 for the same ratio based on the emissions inventory values of NMOC and NO_x (ratios are in molar units of carbon and NO_x). Application of a simple box model using the emissions data yielded good agreement between the predicted and observed NO_x concentrations but the predicted anthropogenic VOC concentration (99 ppbC) was about five times less than the observed concentration (491 ppbC). In another recent study[5], similar NMOC/NO_x ratios were computed for 22 cities in the eastern and central U.S. from 1375 samples of ambient NMOC and NO_x measurements taken specifically in central business districts. The NMOC measurements were based on analyses of the ambient air samples by two independent state-of-the-art techniques. The NO_x data are also considered to be of state-of-the-art accuracy. The results of the ratio NMOC/NO_x for the 22 cities are summarized in Table II. The median values for the 22 cities range between 8.3 and 50.0 (ppmC/ppm), with a median of medians values for all cities of 13.9. For comparison Table III shows the values of the NMOC/NO_x ratio for the five eastern U.S. urban counties with the highest emission flux of NMOC, and five counties with the highest emission flux of NO_x. These ratios are based on gridded precursor emission values extracted from the NAPAP 4.2 inventory and range between 1.49 and 8.25 with the means and medians of the two sets ranging between 3 and 5. These ratios are about 3 to 5 times smaller than 13.9, indicating once again that the VOC emissions in the inventories for urban areas may be underestimated.

The Mass Balance Method for Estimating Urban Emissions

The mass balance method has been used in past studies[6,7] to estimate changes in the mass flow rate of given pollutants between two crosswind sections of a pollutant plume as a result of plume kinetics (chemistry and dry deposition). In these applications the contribution of pollutant mass by primary emissions was either assumed known or was not a factor (e.g., contrasting two cross-sections, both downwind of the source region). In principle, by comparing the mass inflow rate of a given pollutant into an urban source area with the corresponding mass outflow rate just downwind of the source, an estimate can be made of the source contribution (i.e., the primary emission) of the pollutant. The direct difference between these two mass flow rates

Table II. Median ambient urban* $NMOC/NO_x$ concentration ratios during 1984.

EPA Region	Site	Ratio (No. of data)
III	Philadelphia	19.6 (45)
	Wilkes Barre	14.3 (53)
	Richmond	10.5 (62)
	Washington	9.4 (54)
IV	Memphis	13.9 (35)
	Chattanooga	16.8 (37)
	Charlotte	10.4 (55)
	Birmingham	11.7 (51)
	Atlanta	10.5 (52)
	Miami	13.3 (15)
	W. Palm Beach	14.3 (60)
V	Akron	12.8 (49)
	Cincinnati	9.1 (51)
	Indianapolis	8.3 (50)
VI	Beaumont	25.3 (45)
	Clute	23.7 (52)
	Dallas	16.0 (69)
	El Paso	15.3 (60)
	Fort Worth	11.6 (58)
	W. Orange	50.0 (41)
	Texas City	37.7 (52)
VII	Kansas City	-
Median of Medians		13.9 (21)

* In the Central Business District

Table III. $NMOC/NO_x$ emissions ratios of urban counties (based on NAPAP 4.2 emissions inventory).

Urban Counties with highest VOC Emissions Flux:

County	Ratio
New York, N.Y.	3.15
Queens, N.Y.	3.93
Baltimore City MD	8.25
Philadelphia, PA.	3.70
Richmond, N.Y.	4.97
Mean	4.80
Median	3.93

Urban Counties with highest NO_x Emissions Flux:

County	Ratio
New York, N.Y.	3.15
Hudson, N.J.	1.49
Queens, N.Y.	3.93
Union, N.J.	2.91
Philadelphia, PA.	3.70
Mean	3.04
Median	3.15

is, in fact, equal to the species emission rate if the meteorology is in steady state (e.g., constant wind field, mixing height, etc.), and if the pollutant is a conservative species (chemically inert), and nondepositing. In a dynamic and non-uniform meteorological environment, the change in the pollutant mass flow rate between urban upwind and downwind sections will not only be due to urban primary emissions but also to mass exchange at the top and sides of the urban plume, deposition losses at the surface, and chemical transformations within the plume. In such cases, the primary emission contribution may be isolated by separately estimating the contribution of these secondary effects through the use of an appropriate transport/transformation/removal model. It is important, however, to recognize that the estimation of these secondary effects must necessarily be based on some assumed primary emission input to the model. Such primary emission input may be based either on the emission inventory (catch 22!), or may be inferred iteratively in the model application to match the sum of the observed change in the upwind/downwind mass flow rates and the net sink due to all secondary effects. It is advisable to select situations for which the magnitude of the secondary effects is negligible (ideally) or, secondary effects is negligible (ideally) or, at least, small so that the difference between the inflow/outflow mass accounts directly for most of the emission mass.

Irrespective of the magnitude of the secondary effects and the need for the model application, there is a fundamental need in the implementation of the mass balance method to estimate the mass flow rates across one or more crosswind vertical planes. The method for doing this is illustrated below for the case of a conservative species in a uniform, steady meteorological environment. Subsequently, the significance of non-simple meteorology and non-conservative species kinetics will be considered. This illustration is focused on the urban source scenario. The discussion below is based on White et al., 1983. Consider the following scenario for a flow leaving an urban source complex (Figure 5). The local mean flow field is assumed to be spatially uniform, both horizontally and vertically, and locally steady. The urban plume spreads vertically within a mixed layer of uniform and steady "background" chemical composition. (This will not be the case when the background is chemically changing, or being diluted by entrainment of chemically different air from aloft as when the mixing layer is growing in the mid-morning period, or when the background is being modified by removal processes.)

In Figure 5 the primary mass emission rate (Q_i) of any arbitrary species i and the wind speed (U) are shown as functions of time merely to reflect that their values may vary diurnally and seasonally. They are, however, assumed to be temporally constant for the duration of a specific mass balance experiment (for which Q can be considered quasi-stationary).

The following expression describes the primary emission rate in this idealized scenario:

$$Q_i^* = \bar{U} \int_0^{\infty} \int_{-\infty}^{\infty} (\overline{C_i} - \overline{C_{i,bg}}) dy dz \qquad (1)$$

where $\overline{C_i}$ and $\overline{C_{i,bg}}$ are the total and background concentrations respectively. This approximation applies to any source group in which the wind speed $\bar{U}$ over the time of sampled emission is constant. White et

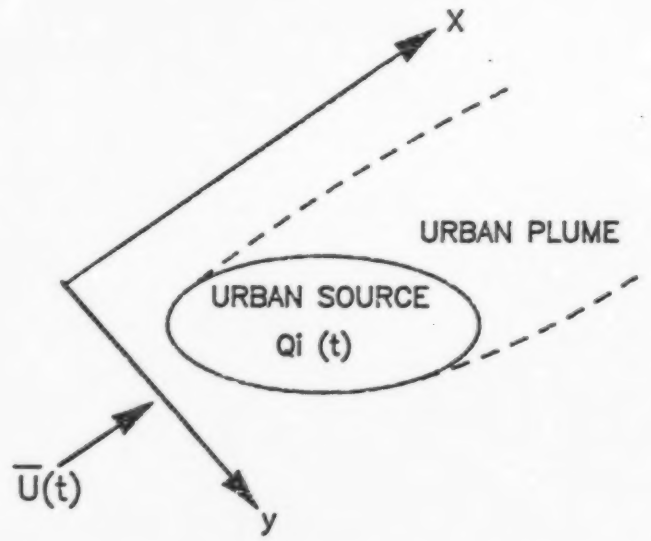

Figure 5. Surface projection of uniform horizontal flow influenced by an urban source

al., 1983, refers to the quantify on the right hand side of (1) as the virtual emission rate, Q_i^* of species i. It represents the fraction of emission of species, i, which would be determined at downwind distance, x, after the emissions have undergone deposition, chemical transformation, and dilution. Therefore, for SO_2 and other primary emissions, Q_i^* will be less than the actual emission rate Q_i, while for secondary product species such as O_3, Q_i^* will be greater than their primary emission rate (zero for O_3).

The difference between Q_i and $Q_i^*(x)$ must represent the net effect of all intervening sink processes affecting the concentration from the source region to x. Thus,

$$Q_{si}(x) = Q_i - Q_i^*(x) \qquad (2)$$

and for a conservative species, Q_i^* is not a function of x and thus $Q_i = Q_i^*$. Note that Q_{i*} is the primary emission rate aggregated for the urban area. Together, Q_i^* and Q_{si} can provide an estimate of Q_i which must then be used for comparison with Q_{EIi}, the emission rate according to the emission inventory.

While this approach is promising, it must be demonstrated that Q_i^* and Q_{si} are measurable or semi empirically determined quantities. Figure 6 is a schematic which defines the parameters of the mass balance approach for a primary pollutant specie. The current emission inventory estimate is Q_{EI} and is qualitatively indicated as small compared to Q_i. The goal of the approach is the determination of Q_i, the aggregate anthropogenic emission of arbitrary species i from the urban source region. (Hereafter, the subscript i will be dropped for convenience.)

There are obviously differences in the magnitude of Q^* for different pollutant compounds, depending on their reactivity, surface uptake and magnitude of the background values. Confidence in the use of the mass balance approach will be greatest for the situation in which Q_s is small relative to Q. However, Q_s is difficult to determine directly and will typically require the use of theoretical or modeling approaches. Therefore modeling "noise", DQ_s, will necessarily be introduced and it should be clear that due to these model uncertainties, the smaller the relative magnitude of Q_s relative to Q, the more "exact" will be the estimated emissions from the mass budget approach. The modeling uncertainties derive from the obvious contributions of measurement "noise" as well as a uncertainties in the chemical modeling due to the requirement to use highly condensed chemical mechanisms and approximate rate constants for the complex ambient air mixtures. Clearly, the mass balance approach achieves greatest potential accuracy when the relative magnitude of DQ_s is small compared to Q_s, or what is better, when the magnitude of Q^* is closest in value to Q. Field measurements to determine Q^* will contain the usual measurement errors, DQ^*, due to sampling errors arising from subgrid scale variations, instrument response, etc. The mass balance technique will require such errors to be much less than Q^*.

Figure 7 illustrates another property of the mass budget approach to be considered. The relative magnitude of Q^* to Q_s will decrease with increasing distance from the downwind edge of the urban source region. This is simply because the role of removal, transformation, and dispersion will increase with x, and since Q is fixed, Q^* must decrease. Additionally, DQ_s will increase commensurately and the resulting confidence in the mass balance technique (Eq. 2) will diminish. There is, of course, the need to measure Q^* far enough downwind of the emissions area so that the pollutants can disperse vertically to heights for which sampling, if performed by aircraft, is possible. The selection of optimum sampling distance is therefore an experiment design problem. It is quite clear that not all meteorological conditions will be suitable for mass budget studies. Sampling platforms and sampling methods have limitations which must be recognized and, moreover, the sampling strategy does require a finite time period to complete. Remote sensing systems such as lidars, sodars, cospecs, etc., provide current technical capabilities in obtaining requisite measurements of key parameters. For example, airborne lidar systems are available to provide real time information on the width and composition of the urban plume, and with range resolution can be used to provide strategic operational information to the other sampling aircraft platforms making in situ measurements. Doppler sodar systems provide detailed wind measurements for determining the air flow fields. As a practical measure, it would be necessary to be selective of meteorological conditions for which relatively steady conditions prevail, for which the mixed layer is and remains fairly shallow over the duration of the experiment, and for which fairly sizeable emissions occur. Further, the wetness of the surface between the sources and x will complicate the parameter relationship of models which governs the quantification of the losses of some pollutants at the surface by deposition processes. Overcast conditions are desireable to reduce the amount of solar radiation and therefore reduce the amount of photochemical conversion of the primary emissions. It may be possible to use the mass balance approach to determine the emissions for the afternoon commuter traffic period. In this situation, the outflow from the urban area may enter

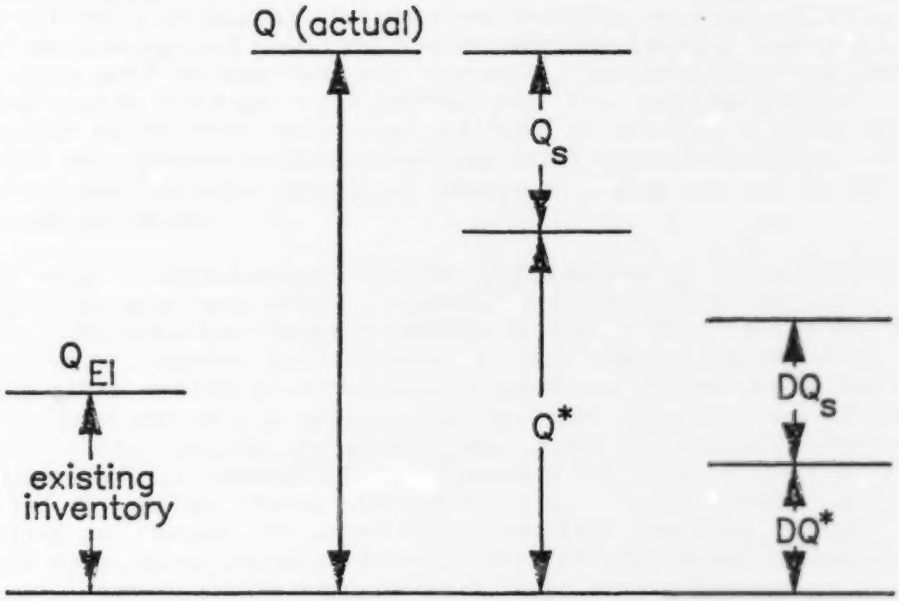

Figure 6. Parameters of the mass balance approach

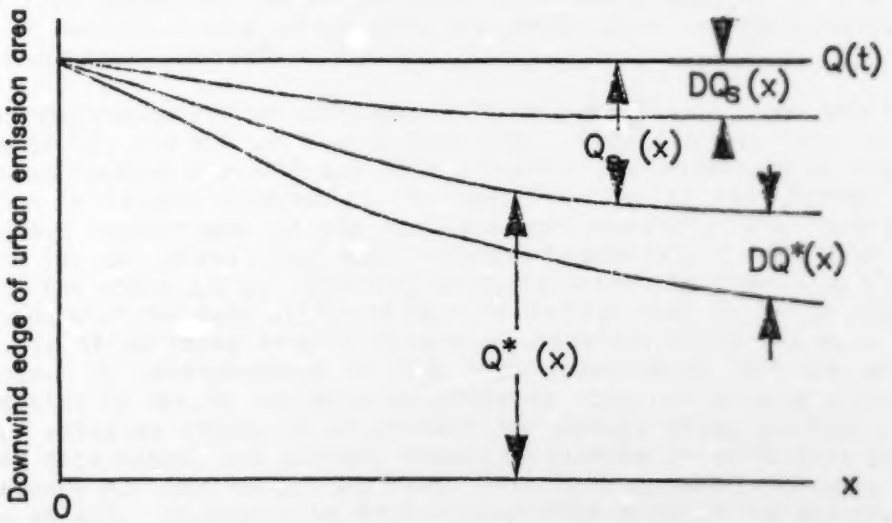

Figure 7. Downwind variation of mass flow parameters for a primary pollutant.

into a mixed layer whose height is now considerably shallower than during the afternoon (winter/fall condition), and moreover, sunlight intensity is strongly reduced dropping to zero at sunset. Operational difficulties at dusk will be more difficult of course. Accurate and detailed measurements to characterize the meteorology and pollutant fields over the temporal and spatial domain of the study will be required, and obviously, suitable sampling instrumentations and mobile (surface and airborne) platforms must be properly deployed. Instrumented helicopters have been utilized in previous studies over urban areas that have permitted nearsurface pollutant characterization. Obviously, the list of observational degrees of freedom are large and need to be carefully limited and optimized.

The mass balance approach can be complimented by Lagrangian studies of tagged air parcels into which a specific source type of emissions has been injected. The detailed characterization of and changes to the pollutants in this air parcel during their transit to the sampling plane from specific sub-urban scale sources provide useful diagnostic information on the magnitude of the Q_S term and on the accuracy of the model determination of the Q_S and DO_S terms. These special emissions areas might include major roadway interchanges located far upwind of the downwind sampling plane, or for major industrial non-mobile source complexes, etc. These studies will provide information on changes in chemical composition and the magnitude of the pollutant mass gains/losses. It will provide the means to separate those emissions of mobile origin from industrial and other sources.

Tracers and parcel markers are currently available which provide the means to conduct these Lagrangian experiments. Methods which utilize pollutant-to-tracer ratio techniques and fingerprinting of specific source types could be incorporated into the experimental design where possible to provide information on emission rates from sub-urban source regions for which inventory uncertainties might be expected to be large. The ratio of various species of VOCs from mobile sources to the acetylene content appears to be a promising method of mobile source fingerprinting which provides interpretive aid to these diagnostic studies[8].

The magnitude of the emissions will be variable in time; point and area sources of NO_x and VOC will vary diurnally. Figure 8 describes the temporal allocation factors for NO_x and VOC; clearly, the magnitude of the diurnal variation is large. Obviously, the consideration of the diurnal variation is a design requirement of the mass balance approach. The straightforward solution is, of course, the mass balance determination of Q for different times of the daily cycle. Clearly, characterizing the diurnal variation is a major aspect of the feasibility study. An initial step in judging feasibility is the use of existing data to determine emissions using the mass flow rate technique. In consideration of the major expense of and the operational difficulties to obtain reliable measurements required to make accurate estimates of emission rates, it is prudent to conduct pilot studies using both existing data bases, and current models to examine in sufficient detail, the requirements for mass budget studies. This is discussed in greater detail by Gillani et al[1]. It should be noted though that none of the existing ambient data bases were collected with the objective of reconciling source emissions with ambient data and therefore may be incomplete for this purpose.

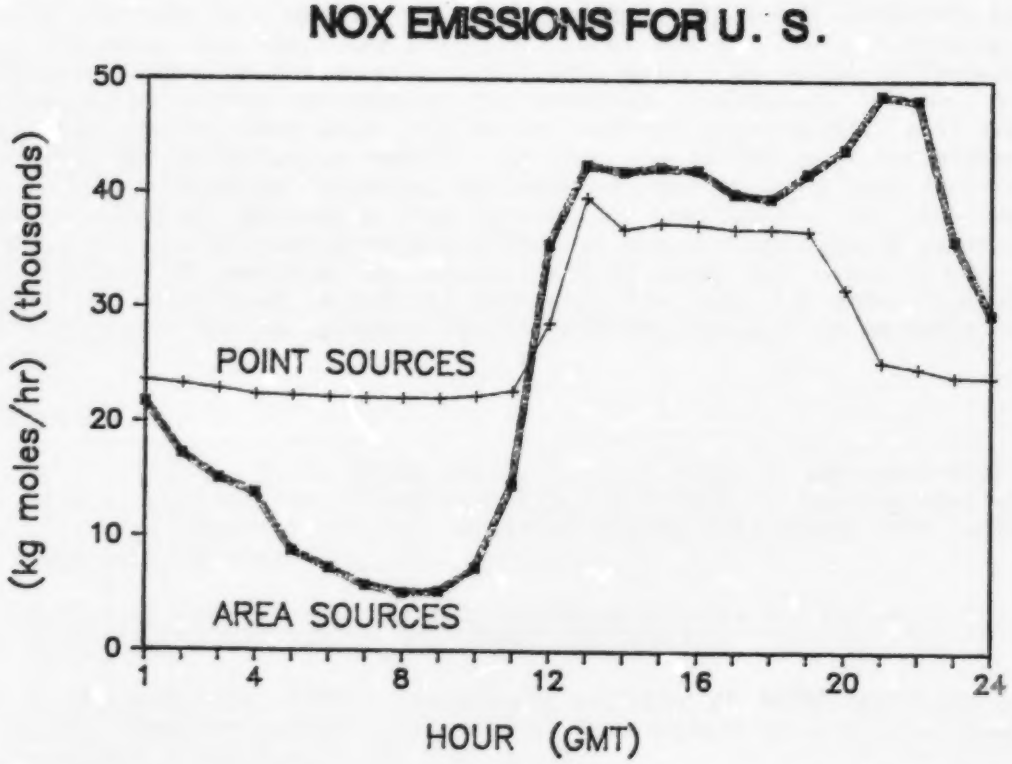

Figure 8. Diurnal variation of NOX from NAPAP 4.2 emissions inventory.

SUMMARY AND CONCLUSIONS

Improvements are continuously being made to emission inventories, both raw data corrections/updates and methodology improvements. Since these improvements have significant impact on emissions inputs to Eulerian regional scale models there is a real need to determine the accuracy of the emission inventories as well as the uncertainty of various components used in estimating emissions. In addition, ambient measurement data indicate a potential underestimation of VOC emissions, however, these point measurements are not necessarily representative of larger scale emissions.

This paper has proposed a mass balance approach as a potential means of obtaining an independent estimate of area wide VOC and NO_x emissions which can be used to determine some level of accuracy of existing emission estimates in urban areas. This ambient measurement technique uses measured air concentration data downwind and downwind of an urban area to estimate emissions for the area over a specified unit of time. The net effect of all processes influencing the concentration from the emitting sources to the point of downwind

measurement must be accounted for and underlying uncertainties quantified. The feasibility of this approach is currently being explored by analyzing existing ambient measurement data bases.

We conclude that confidence in the accuracy of current emissions inventory estimates are low. Certainly, the bias and the "noise" arising from both inadequacies in the emission input data as well as in the differences in methodologies adopted to develop the emission inventories is very large. Such inaccuracies, when used in urban or regional scale models, will lead to erroneous and inconclusive results. In fact, due to the great uncertainty in the emission inventory accuracy, the modeling results might well lead to air pollution control strategies that are either ineffective, or, even worse, wrong. The mass balance technique offers one possible approach to determining the accuracy of emission estimation methodologies for urban areas. The problem is significant enough to emphasize the need for more research to determine an effective approach for quantifying accuracy of emission inventories.

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